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71 Applicant: **WILSON GREATBATCH LTD.**  
**10,000 Wehrle Drive**  
**Clarence New York 14031 (US)**

72 Inventor: **Takeuchi, Esther S.**  
**1260 North Forest Road**  
**Williamsville, New York 14221 (US)**  
Inventor: **Lelsing, Randolph A.**  
**177 Roesch Avenue**  
**Buffalo, New York 14207 (US)**

74 Representative: **Cropp, John Anthony David et al**  
**MATHYS & SQUIRE**  
**10 Fleet Street**  
**London, EC4Y 1AY (GB)**

54 Metaloxide composite-cathode material for high energy density batteries.

57 An electrochemical cell incorporating a cathode material comprising a mixed oxide of vanadium, silver and copper. The cathode materials of this invention are formed by the chemical addition, reaction, or otherwise intimate contact of various mixed oxides and/or metal elements during thermal treatment in mixed states. A preferred material comprises a composite metal oxide matrix formed as the thermal decomposition and reaction product of a matrix of vanadium oxide and at least decomposable compounds of copper and silver.

EP 0 618 630 A1

## BACKGROUND OF THE INVENTION

## 1. Field of the Invention

This invention relates to the art of electrochemical cells and more particularly to a new and improved electrochemical cell and cathode therefor comprising a Group IA anode and a composite metal-metal-metal oxide cathode.

Light metals have exceptionally high energy density when employed as the anode material in electrochemical cells owing to their low atomic weight and high standard potential. This high chemical activity of light metal anode material requires the use of a nonaqueous electrolyte and a cathode which meets the rigorous requirements for such a cell. Most cathode materials are too readily soluble in a nonaqueous electrolyte and, thereby, reduce the useful capacity of such an electrode after storage. The cathode material of the present invention uses a mixed-metal oxide containing copper, silver, and vanadium as an electrode material for application as a cathode in a lithium battery. This provides a new and distinct cathode material having the general formula  $\text{Cu}_x\text{Ag}_y\text{V}_2\text{O}_z$ , also referred to herein as CSVO.

## 2. Prior Art.

It is known to use metal oxide as cathode materials in nonaqueous electrochemical cells. For example, U.S. Patent No. 4,310,609 to Liang, et al., which is assigned to the assignee of the present invention and incorporated herein by reference, discloses the use of a composite cathode material including  $\text{V}_2\text{O}_x$  wherein  $x = 5$  combined with one or more of  $\text{Ag}_2\text{O}_x$  wherein  $x = 1$  to  $1$ ;  $\text{CuO}_x$  wherein  $x = 0$  to  $1$ ; and  $\text{MnO}_x$  wherein  $x = 1$  to  $3$ . The composite material is described as a metal oxide-metal oxide, a metal-metal oxide, or a metal-metal oxide-metal oxide. A preferred embodiment of this cathode material has the formula  $\text{AgV}_2\text{O}_{5.5}$ , also referred to herein as SVO.

While this prior art battery material works well, the cathode material of the present invention provides an increased gravimetric energy density and an increased pulse voltage delivery capacity. This makes the cathode material of the present invention particularly useful for implantable medical applications. The CSVO material of the present invention is also an improvement over SVO cathode material in savings on the expense of the silver starting material.

## SUMMARY OF THE INVENTION

This invention relates to electrochemical cells comprising an anode of a Group IA metal and a cathode of a composite material prepared by the chemical addition, reaction, or otherwise intimate contact of several metal oxides, metal or metal oxide/elemental metal combinations, preferably during thermal treatment, sol-gel formation, chemical vapor deposition or hydrothermal synthesis in mixed states.

## OBJECTS OF THE INVENTION

It is an object of the present invention to provide a new and improved electrochemical cell having relatively high energy density, discharge capacity, reduced voltage delay under high rate applications, and a wide operating temperature range.

It is a further object of this invention to provide such an electrochemical cell of high reliability and utility even after prolonged storage.

It is another object of this invention to provide such an electrochemical cell having a relatively high open circuit voltage and current capacity.

It is still another object of this invention to provide an electrochemical cell having an oxidisable active anode material and a cathode material combining various metal oxides or oxide/elemental metal combinations prepared by the method of the present invention.

According to the present invention, there is provided an electrochemical cell having an anode of a Group IA metal which is electrochemically oxidisable to form metal ions in the cell upon discharge to generate electron flow in an external electrical circuit connected to the cell; a cathode comprising a mixed metal oxide of vanadium, copper and silver; and an ionic conductive electrolyte solution operatively associated with the anode and cathode.

The invention also provides a cathode for use in the cell, the cathode comprising a mixed metal oxide of vanadium, copper and silver.

In a preferred embodiment, the mixed metal oxide satisfies the general formula



wherein  $0.01 > x > 1.0$  and  $0.01 > y > 1.0$  and preferably  $x$  is equal to or less than  $y$ . More preferably  $0.08 > x > 0.5$  and  $0.50 > y > 0.67$ . In one embodiment, the value for  $z$  is preferably such that  $3.5 < z < 6.5$  and in another  $z$  is preferably such that  $5.01 < z < 6.5$ .

5 The invention also provides a method of forming the cathode wherein the mixed metal oxide is formed by forming a reaction product from vanadium oxide and decomposable compounds of silver and copper. The vanadium oxide is preferably derived from ammonium vanadate and has the formula  $\text{V}_2\text{O}_z$  where  $z$  is less than or equal to 5. The decomposable silver compound is preferably selected from silver nitrate, silver nitrite, silver carbonate and salts of silver oxyanions. The decomposable copper compound is preferably copper nitrate. Alternatively the mixed oxide may be obtained by mixing together oxides of vanadium, silver and copper.

The invention will now be described in greater detail with reference to preferred embodiments thereof and with the aid of the accompanying drawings wherein

FIG. 1 is a voltage-time plot for a cell according to one embodiment of the present invention.

15 FIG. 2 is a voltage-time plot comparing a cell according to one embodiment of the present invention and a cell made according to the prior art.

FIG. 3 is a voltage-cumulative capacity plot for a cell according to one embodiment of the present invention showing open circuit voltage and minimum pulse voltage.

## DETAILED DESCRIPTION OF THE INVENTION

20 The electrochemical cell of the present invention comprises an anode of a metal selected from Group IA of the Periodic Table of the Elements, including lithium, sodium, potassium, etc., and their alloys and intermetallic compounds including, for example, Li-Si, Li-Al, Li-B and Li-Si-B alloys and intermetallic compounds. The form of the anode may vary, but typically, it is made as a thin sheet or foil of the anode metal, and a current collector having an extended tab or lead affixed to the anode sheet or foil.

25 The electrochemical cell of the present invention further comprises a cathode of electronically conductive composite material which serves as the other electrode of the cell. The electrochemical reaction at the cathode involves conversion of ions which migrate from the anode to the cathode into atomic or molecular forms. The composite cathode material of the present invention comprises at least one metal oxide and at least a first and a second metals, or a mixture of a first and a second metals or their metal oxides incorporated in the matrix of the host metal oxide.

30 The cathode material of this invention can be constructed by the chemical addition, reaction, or otherwise intimate contact of various metal oxides and/or metal elements, preferably during -- thermal treatment, sol-gel formation, chemical vapor deposition or hydrothermal synthesis in mixed states. The material thereby produced contains metals and oxides of vanadium, silver and copper.

35 According to the method of the present invention, readily decomposable compounds of the relevant metals are thermally treated so as to effect the rapid preparation of the oxides or the respective metal elements themselves to be utilized further in the preparation of suitable cathode materials. Such readily decomposable materials include, but are not limited to, those classes of compounds known as nitrates, nitrites, carbonates, and/or salts of metal oxyanions e.g. ammonium salts.

40 The precursor material (i.e., nitrates, nitrites, carbonates, metal ammonium compounds, etc.) may be decomposed in a combined state or individually decomposed and thereafter combined in an oxide/decomposable metal salt compound and subsequently decomposed to form the cathode composite matrix. Such composite materials may be pressed into a cathode pellet with the aid of a suitable binder material and a material having electronic conduction characteristics such as graphite. In some cases, no binder material or electronic conductor material is required to provide a similarly suitable cathode body. Further, some of the cathode matrix samples may also be prepared by rolling, spreading or pressing a mixture of the material mentioned above onto a suitable current collector such as Exmet wire mesh. Cathodes prepared as described above may be in the form of one or more plates operatively associated with at least one or more plates of anode material, or in the form of a strip wound with a corresponding strip of anode material in a structure similar to a "jellyroll". The cathode is separated in both cases from the Group IA anode material by a suitable separator material such as a porous glass woven or polypropylene or polyethylene microporous material.

45 Preferred cathode composites are prepared by thermally decomposing a vanadium salt, suitably ammonium metavanadate to produce vanadium pentoxide. A decomposable metal salt, suitably the nitrates of a second metal and a third metal, is then added to the vanadium pentoxide, thoroughly mixed therewith and thereafter ignited. The second and third metals are most preferably silver and copper. The resultant composite cathode includes  $\text{V}_2\text{O}_5$  wherein  $z \leq 5$  combined with  $\text{Ag}_2\text{O}$ , wherein  $z = 0$  to 1 and  $\text{CuO}$  wherein  $z = 0$  to 1 to provide a new and distinct material having the formula  $\text{Cu}_x\text{Ag}_y\text{V}_z\text{O}_z$ , (CSVO). Thus, the composite cathode material

may be described as a metal oxide-metal oxide-metal oxide, a metal-metal oxide-metal oxide, or a metal-metal-metal oxide and the range of material composition found for  $\text{Cu}_x\text{Ag}_y\text{V}_2\text{O}_z$  is preferably about  $0.01 > x > 1.0$  and about  $0.01 > y > 1.0$ . A typical form of CSVO is  $\text{Cu}_{0.16}\text{Ag}_{0.67}\text{V}_2\text{O}_z$  which is single phase and is characterized by an exothermic transition at  $537^\circ\text{C}$  in the differential scanning calorimetry data and d-spacings of 4.36, 3.75, 3.59, 3.45, 3.20, 3.08, 3.03, and 2.97 in the X-ray powder diffraction pattern for the sample. The CSVO synthesized as described above displays a bulk density of 1.5 g/mL and displays a characteristic sloping voltage versus time curve for the discharge of a Li/CSVO cell (FIG. 1), prepared as described in detail presently. The sloping discharge curve is of particular importance for batteries in implantable medical applications where a state of charge indication extrapolated from cell voltage is needed. Another form is  $\text{Cu}_{0.6}\text{Ag}_{0.6}\text{V}_2\text{O}_z$ .

The electrochemical cell of the present invention further comprises a nonaqueous, ionic conductive electrolytic solution of Group IA metal salt operatively associated with the anode and the cathode. The electrolytic solution serves as a medium for migration of ions between the anode and cathode during cell electrochemical reactions. The nonaqueous solvents suitable for the invention are chosen so as to exhibit those physical properties necessary for ionic transport (low viscosity, low surface tension, and wettability). The nonaqueous solvent of the electrolyte may be any one or more of the organic solvents which is substantially inert to the anode and cathode electrode materials, such as tetrahydrofuran, propylene carbonate, methyl acetate, acetonitrile, dimethyl sulfoxide, dimethyl formamide, dimethyl acetamide, 1,2-dimethoxyethane and others. The nonaqueous solvent also may be one or a mixture of more than one of the inorganic solvents which can serve as both a solvent and a depolarizer, such as thionyl chloride, sulfur chloride, selenium oxychloride, chromyl chloride, phosphoryl chloride, phosphorous sulfur trichloride, and others. The Group IA metal salt of the nonaqueous electrolytic solution may be chosen from, for example, lithium halides, such as LiCl and LiBr, and lithium salts of the  $\text{LiMX}_n$  type, such as  $\text{LiAlCl}_4$ ,  $\text{Li}_2\text{Al}_2\text{Cl}_6\text{O}$ ,  $\text{LiClO}_4$ ,  $\text{LiAsF}_6$ ,  $\text{LiSbF}_6$ ,  $\text{LiSbCl}_6$ ,  $\text{Li}_2\text{TiCl}_6$ ,  $\text{Li}_2\text{SeCl}_6$ ,  $\text{Li}_2\text{B}_{10}\text{Cl}_{10}$ ,  $\text{Li}_2\text{Bi}_{12}\text{Cl}_{12}$ , and others. Alternatively, the corresponding sodium or potassium salts may be used.

When the mechanical structure or configuration of the cell requires, a separator can be employed to provide physical separation between the anode and the cathode current collectors. The separator is of electrically insulative material to prevent an internal electrical short circuit in the cell between the anode and the cathode current collectors. The separator materials also must be chemically unreactive with the materials of the anode and cathode current collectors and both chemically unreactive with and insoluble in the electrolytic solution. In addition, the separator material must have a degree of porosity sufficient to allow flow therethrough of the electrolytic solution during the electrochemical reaction of the cell. Illustrative separator materials include nonwoven glass, polytetrafluoroethylene (PTFE), glass fiber material, ceramics, and PTFE membranes commercially available under the designations ZITEX (Chemplast Inc.), polypropylene membranes, commercially available under the designation CELGARD (Celanese Plastic Company Inc.), and methyl acrylate plastic, commercially available under the designation DEXIGLAS (C.H. Dexter, Div. Dexter Corp.). The form of the separator typically is a sheet which is placed between the anode and the cathode of the cell in a manner preventing physical contact between the anode and cathode, and such contact also is prevented when the combination is rolled or otherwise formed into a cylindrical configuration having a jellyroll shape.

The electrochemical cell of the present invention operates in the following manner. When the ionic conductive electrolytic solution becomes operatively associated with the anode and cathode of the cell, an electrical potential difference is developed between terminals operatively connected to the anode and cathode. The electrochemical reaction at the anode includes oxidation to form metal ions during discharge of the cell. The electrochemical reaction at the cathode involves conversion of ions which migrate from the anode to the cathode into atomic or molecular forms. It is observed that the systems of this invention have a wide operating temperature range of about  $-20^\circ\text{C}$  to  $+70^\circ\text{C}$ . Advantages of the CSVO cathode material according to the present invention include a high delivered capacity for the intercalation of lithium and reduced voltage delay under high rate applications, such as in batteries for implanted cardiac defibrillators, together with the cost saving resulting from the reduced amount of silver as starting material.

The electrochemical cell according to the present invention is illustrated further by the following examples.

#### Example 1

##### Preparation of $\text{Cu}_{0.16}\text{Ag}_{0.67}\text{V}_2\text{O}_z$

Copper-Silver Vanadium Oxide (CSVO) was synthesized via a solid-state reaction of thermally decomposable salts of copper and silver with vanadium pentoxide. The oxygen content in  $\text{Cu}_{0.16}\text{Ag}_{0.67}\text{V}_2\text{O}_z$  is designated by z since the exact stoichiometry of oxygen depends on the conditions and method used in preparation of the material.

Commercially available ammonium vanadate,  $\text{NH}_4\text{VO}_3$  (Cerac, 99.99%, -80 mesh) was thermally decom-

posed to vanadium pentoxide,  $V_2O_5$ , in an air furnace at elevated temperatures. Evidence for the complete decomposition was based upon the distinct lack of  $NH_3(g)$  and the comparison of product yield to the theoretical yield for  $V_2O_5$ .

Silver nitrate,  $AgNO_3$  (16.73 g, 0.098 mol) and copper(II) nitrate hydrate,  $Cu(NO_3)_2 \cdot 3H_2O$  (5.68 g, 0.024 mol) were dissolved in 25 mL of deionized/distilled water. The aqueous salt solution was added to the previously prepared solid vanadium pentoxide,  $V_2O_5$  (26.74 g, 0.147 mol), and the resulting slurry heated to 80 to 120°C to evaporate all of the water. During this time the slurry was mixed intermittently until the sample became a dry powder. This powder was ground to thoroughly mix the components. The solid was heated at 230°C under an air atmosphere for at least 30 minutes, and mixed again. The temperature of the oven was then increased to 260°C for at least 2 hours, followed by heating at 300°C for at least 16 hours. The material was then ground again, and heated at 375°C for not less than 24 hours. Upon cooling, the material was used without further preparation.

#### Example 2

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##### Preparation of $Cu_{0.5}Ag_{0.5}V_2O_z$

Silver nitrate,  $AgNO_3$  (16.63 g, 0.098 mol) and copper(II) nitrate hydrate,  $Cu(NO_3)_2 \cdot 3H_2O$  (23.66 g, 0.098 mol) were dissolved in 30 mL of deionized/distilled water. The aqueous salt solution was added to solid vanadium pentoxide,  $V_2O_5$  (35.62 g, 0.196 mol) and the material was synthesized as described in Example 1.

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#### Example 3

##### Preparation of $Cu_{0.16}Ag_{0.87}V_2O_z$ from metal oxides

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$Cu_{0.16}Ag_{0.87}V_2O_z$  may be synthesized from metal oxides. Silver oxide,  $Ag_2O$  (2.14 g, 0.009 mol) and copper(II) oxide,  $CuO$  (0.35 g, 0.004 mol) were mixed as dry powders and added to solid vanadium pentoxide,  $V_2O_5$  (5.00 g, 0.028 mol). This dry powder sample was mixed well and thermally treated as described in Example 1. The metal oxides may also be taken up as a slurry in aqueous or nonaqueous solvent, mixed thoroughly and dried as described in Example 1. Additional salts may also be used for the synthesis of CSVO materials. Examples of silver and copper salts for the synthesis include, but are not limited to, classes of salts known as nitrites, acetates, and carbonates, as well as the above-mentioned nitrates and oxides. Copper materials may be used in either the copper(II), copper(I) or copper(0) oxidation state. In addition,  $AgVO_3$  or other  $Ag_xVO_z$  precursors may be combined with  $V_2O_z$  and a salt of copper or copper metal to form the CSVO material. Likewise, a silver or salt or silver metal may be combined with a  $Cu_xVO_z$  precursor and  $V_2O_z$  to form CSVO.

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#### Comparative Example 1

##### Preparation of $AgV_2O_z$

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Silver Vanadium Oxide ( $SVO, AgV_2O_z$ ) was synthesized to provide a comparison to the Copper-Silver Vanadium Oxides from Examples 1 to 3. Silver nitrate,  $AgNO_3$  (93.4 g, 0.55 mol) was dissolved in 70 mL of deionized/distilled water. The aqueous salt solution was added to solid vanadium pentoxide,  $V_2O_5$  (100.0 g, 0.55 mol), and the mixture was synthesized as described in Example 1.

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#### Example 4

##### Thermal analysis Of materials

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Differential Scanning Calorimetry (DSC) data was obtained for CSVO samples made according to Examples 1 and 2 and SVO made according to Comparative Example 1. The results for scans from 25°C to 600°C are presented in Table I. It can be readily seen that CSVO materials display different thermal properties than the SVO material, demonstrating that CSVO is a new species, significantly different from SVO.

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TABLE I

Temperature of Thermal Transitions		
$\text{Cu}_{0.16}\text{Ag}_{0.87}\text{V}_2\text{O}_{5.5}$	$\text{Cu}_{0.5}\text{Ag}_{0.5}\text{V}_2\text{O}_{5.75}$	$\text{AgV}_2\text{O}_z$
523°C	542°C	462°C
537°C		540°C
592°C		553°C
		591°C

### Example 5

#### Preparation of test cells

Test cells were constructed having a lithium anode and an electronically conductive composite cathode made according to the present invention, along with an organic electrolyte. The electrolyte used in these cells was comprised of, but should not be limited to, lithium hexafluoroarsenate dissolved in a mixture of propylene carbonate and 1,2-dimethoxyethane. These experimental cells were used to test the ability of CSVO made according to Examples 1 to 3 to intercalate lithium under constant resistance discharge, current pulse, or a combination of these test conditions. In addition, test cells were constructed using SVO made according to Comparative Example 1 to compare to the CSVO materials. The cell design utilized a cathode in the form of a pellet having a length of 3.6 cm, a width of 1.4 cm, and a thickness of about 0.06 cm. The cathode consisted of a mixture of 94% of active material (CSVO or SVO) by weight along with 3% PTFE, 2% graphite, and 1% carbon black. The mixture was pressed onto an expanded metal current collector, and the cathode separated from the lithium anode by a polypropylene separator. Lithium metal (1.4 x 3.6 x 0.08 cm), also in contact with an expanded metal current collector, was placed against the separator facing the CSVO cathode. Both electrodes were surrounded by glass plates and held together by small metal clamps. The electrodes were placed in a glass enclosure and filled with a 1 molar solution of lithium hexafluoroarsenate ( $\text{LiAsF}_6$ ) dissolved in an equal volume mixture of propylene carbonate (PC) and 1,2-dimethoxyethane (DME) as electrolyte. The test cell was capped to avoid the evaporation of DME electrolyte.

### Example 6

#### Discharge of Li/CSVO compared to Li/SVO

The test cells described in Example 5 were discharged at room temperature under a constant 200 ohm load down to a voltage of +1.5 V vs  $\text{Li/Li}^+$ , corresponding to the intercalation of  $\text{Li}^+$  into the cathode material. The cells containing CSVO cathodes displayed an increase in delivered capacity over that seen for silver vanadium oxide (SVO), as listed in Table II. The capacity values in Table II are based on the amount of active material in the cathode. The voltage of a test cell using CSVO from Example 2 is plotted as a function of time during the 200 ohm discharge of FIG. 1. A comparison of the voltage-time results for the discharge of Li/CSVO from Example 2 and Li/SVO from Comparative Example 1 is presented in FIG. 2.

TABLE II

Cathode Material	Capacity	
	to +2.0 V	to +1.5 V
AgV <sub>2</sub> O <sub>z</sub> ,SVO	250 Ah/kg (610 Wh/kg)	300 Ah/kg (690 Wh/kg)
Cu <sub>0.16</sub> Ag <sub>0.67</sub> V <sub>2</sub> O <sub>z</sub>	270 Ah/kg (650 Wh/kg)	310 Ah/kg (710 Wh/kg)
Cu <sub>0.5</sub> Ag <sub>0.5</sub> V <sub>2</sub> O <sub>z</sub>	280 Ah/kg (680 Wh/kg)	330 Ah/kg (760 Wh/kg)

Pulse testing (0.19 Amp) Of experimental cells at room temperature using CSVO from Examples 1 and 2 also demonstrated substantially decreased voltage delay when compared to cells employing SVO from Comparative Example 1.

#### Example 7

#### Preparation and testing of multi-plate batteries

Multi-plate batteries containing cathodes similar in construction to those described in Example 4 were built using CSVO from Examples 1 and 2 and SVO from Comparative Example 1. These batteries contained lithium anodes., 1 M LiAsF<sub>6</sub> PC/DME (50/50) electrolyte, and were hermetically sealed. These cells were discharged via constant current pulse testing at 37°C. Current pulses of 1.5 Amps were applied for 10 seconds in duration followed by 15 seconds of open circuit rest between pulses. These pulses were applied in groups of four, with 30 minutes of open circuit rest between groups. The results of the pulse testing are presented in Table III. The open circuit voltage and minimum voltage for the fourth pulse of each group are plotted in FIG. 3 for a LI/CSVO multi-plate battery containing Cu<sub>0.16</sub>Ag<sub>0.67</sub>V<sub>2</sub>O<sub>z</sub>.

TABLE III

Cathode Material	Capacity	
	to +2.0 V	to +1.5 V
AgV <sub>2</sub> O <sub>z</sub> ,SVO	1436 mAh	1704 mAh
Cu <sub>0.16</sub> Ag <sub>0.67</sub> V <sub>2</sub> O <sub>z</sub>	1471 mAh	1726 mAh
Cu <sub>0.5</sub> Ag <sub>0.5</sub> V <sub>2</sub> O <sub>z</sub>	1545 mAh	1784 mAh

The above detailed description and examples are intended for purposes of illustrating the invention and are not to be construed as limiting.

#### Claims

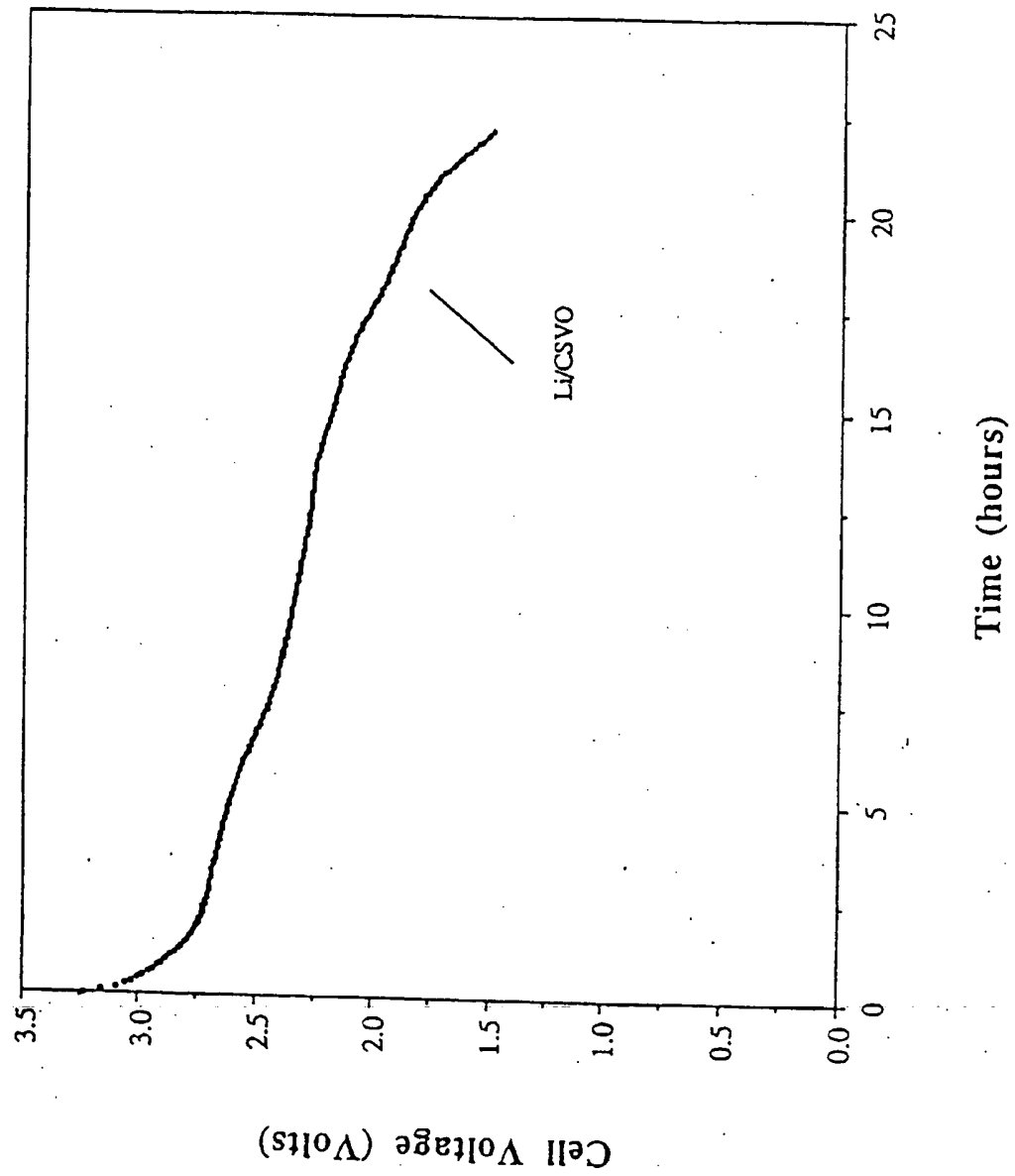
1. A cathode for an electrochemical cell comprising a mixed metal oxide of vanadium, copper and silver.
2. A cathode as claimed in claim 1 wherein the mixed metal oxide has the formula  

$$\text{Cu}_x\text{Ag}_y\text{V}_2\text{O}_z$$
wherein  $0.01 > x > 1.0$  and  $0.01 > y > 1.0$ .
3. A cathode as claimed in claim 2 where in x is equal to or less than y.

4. A cathode as claimed in claim 2 or claim 3 wherein  $0.08 > x > 0.5$  and  $0.50 > y > 0.67$ .
5. A cathode as claimed in any one of claims 2 to 4 wherein  $3.5 < z < 6.5$ .
- 5 6. A cathode as claimed in any one of claims 2 to 4 wherein  $5.01 < z < 6.5$ .
7. A cathode as claimed in any one of claims 2 to 6 wherein  $x$  is 0.16 and  $y$  is 0.67 or  $x$  is 0.5 and  $y$  is 0.5.
8. A cathode as claimed in claim 7 wherein  $z$  is 5.5 when  $x$  is 0.16 and  $z$  is 5.75 when  $x$  is 0.5.
- 10 9. A cathode as claimed in any one of claims 1 to 8 wherein one component of the mixed metal oxide comprises  $V_2O_z$  wherein  $z$  is less than or equal to 5.
10. A cathode as claimed in any one of claims 1 to 9 wherein one component of the mixed metal oxide comprises  $Ag_2O_z$  where  $z$  ranges from about 0 to 1.
- 15 11. A cathode as claimed in any one of claims 1 to 10 wherein one component of the mixed metal oxide comprises  $CuO_z$  where  $z$  ranges from about 0 to 1.
12. A cathode as claimed in any one of claims 1 to 11 which further includes at least one of (a) a binder material, e.g. a fluoro-resin powder, and (b) a conductive additive material, e.g. carbon.
- 20 13. A method of forming a cathode as claimed in any one of claims 1 to 12 wherein the mixed metal oxide is formed by forming a reaction product from vanadium oxide and decomposable compounds of silver and copper.
- 25 14. A method as claimed in claim 13 wherein the vanadium oxide is derived from ammonium vanadate and has the formula  $V_2O_z$  where  $z$  is less than or equal to 5.
15. A method as claimed in claim 13 or claim 14 wherein the decomposable silver compound is selected from silver nitrate, silver nitrite, silver carbonate and salts of silver oxyanions.
- 30 16. A method as claimed in any one of claims 13 to 15 wherein the decomposable copper compound is copper nitrate.
17. A method as claimed in any one of claims 13 to 16 wherein the mixed oxide is formed by a treatment selected from at least one of thermal treatment, sol-gel formation, chemical vapour deposition and hydrothermal synthesis.
- 35 18. A method as claimed in any one of claims 13 to 16 wherein the mixed oxide is formed by a thermal addition reaction or a thermal decomposition reaction.
- 40 19. A method as claimed in any one of claims 13 to 18 which comprises thermally treating a mixture of vanadium pentoxide, silver nitrate and copper nitrate.
20. A method of forming a cathode as claimed in any one of claims 1 to 12 wherein the mixed metal oxide is obtained from oxides of vanadium, silver and copper.
- 45 21. An electrochemical cell having an anode of a Group IA metal which is electrochemically oxidisable to form metal ions in the cell upon discharge to generate electron flow in an external electrical circuit connected to the cell, a cathode as claimed in any one of claims 1 to 12 or obtained by a method as claimed in any one of claims 13 to 20, and an ionic conductive electrolyte solution operatively associated with the anode and cathode.
- 50 22. An electrochemical cell as claimed in claim 21 wherein the electrolyte solution comprises a Group IA metal salt dissolved in a nonaqueous solvent.
- 55 23. An electrochemical cell as claimed in claim 22 wherein the nonaqueous solvent comprises an inorganic solvent or an organic solvent.



Figure 1



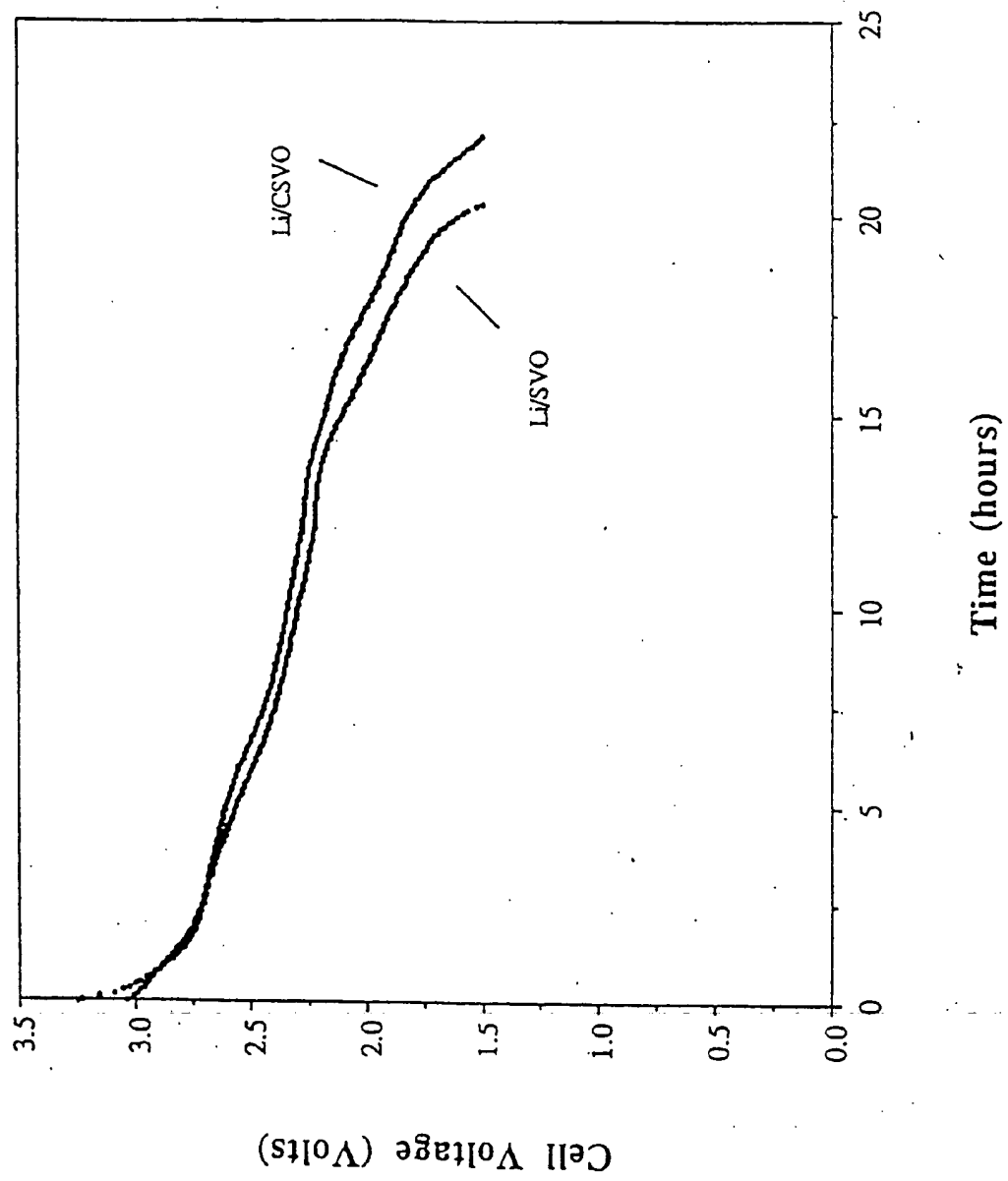


Figure 2

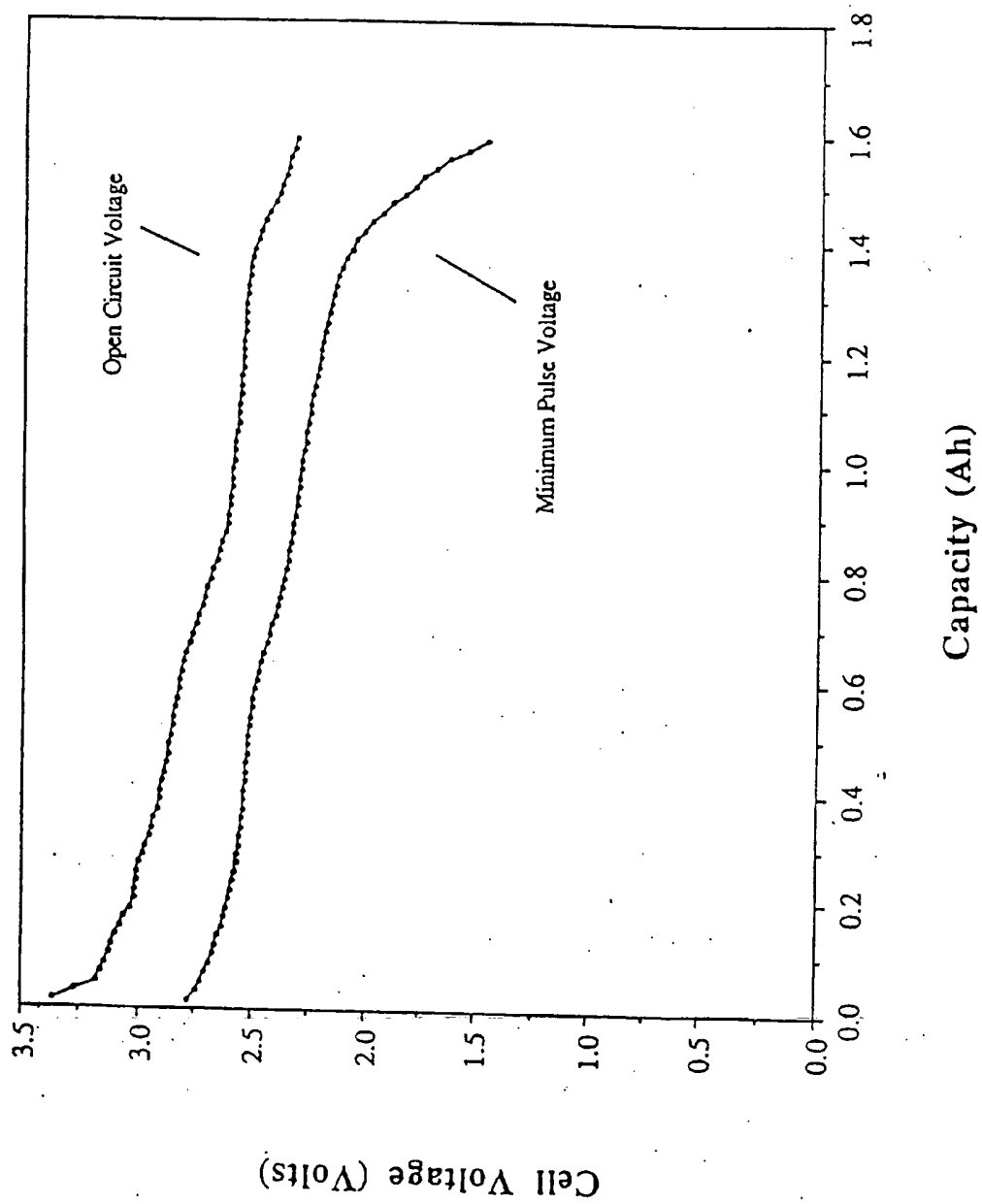


Figure 3



European Patent  
Office

# EUROPEAN SEARCH REPORT

Application Number  
EP 94 30 1910

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. 8)
A	FR-A-2 616 013 (ETAT FRANCAIS) * claims 1,3,4,7 * * page 6, line 8 - line 12 * * page 9, line 14 - line 18 * ---	1	H01M4/48 H01M4/58
D,A	GB-A-2 065 957 (WILSON GREATBATCH) ---		
A	CHEMICAL ABSTRACTS, vol. 116, no. 4, 27 January 1992, Columbus, Ohio, US; abstract no. 24732e, TONOMURA ET AL 'Electrode materials for solid-state batteries, and manufacture method' * abstract * & JP-A-03 194 857 (MATSUSHITA ELECTRIC INDUSTRIAL CO) 26 August 1991 ---		
A	EP-A-0 478 303 (MEDTRONIC INC) ---		
A	JOURNAL OF THE ELECTROCHEMICAL SOCIETY., vol.139, no.11, November 1992, MANCHESTER, NEW HAMPSHIRE US pages 3206 - 3214 F. GARCIA-ALVARADO ET AL 'Synthesis and Electrochemical Study of New Copper Vanadium Bronzes and of Two New V2O5 polymorphs' ---		TECHNICAL FIELDS SEARCHED (Int. Cl. 8) H01M
A	PATENT ABSTRACTS OF JAPAN vol. 8, no. 264 (E-282) (1701) 4 December 1984 & JP-A-59 134 562 (NIPPON DENSHIN DENWA KOSHA) 2 August 1984 * abstract * -----		
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 19 July 1994	Examiner D'hondt, J
<p><b>CATEGORY OF CITED DOCUMENTS</b></p> <p>X: particularly relevant if taken alone Y: particularly relevant if combined with another document of the same category A: technological background O: non-written disclosure P: intermediate document</p> <p>T: theory or principle underlying the invention E: earlier patent document, but published on, or after the filing date D: document cited in the application L: document cited for other reasons A: member of the same patent family, corresponding document</p>			

EP 0 618 630 A1 (1994)